

Introduction: Xenon is the heaviest gas found in significant quantities in natural planetary atmospheres. It would seem the least likely to escape. Yet there is more evidence for xenon escape from Earth than for any element other than helium and perhaps neon. The most straightforward evidence is that most of the radiogenic Xe from the decay of ¹²⁹I (half-life 15.7 Myr) and ²⁴⁴Pu (half-life 81 Myr) that is Earth's birthright is missing. The missing xenon is often attributed to the impact erosion of early atmospheres of Earth and its ancestors. It is obvious that if most of the radiogenic xenon were driven off by impacts, most of the rest of the atmophiles fared the same fate. The other line of evidence is in the nonradiogenic isotopes of xenon and its silent partner, krypton. Atmospheric xenon is strongly mass fractionated (at about 4% per amu) compared to any known solar system source (Figure 1). This is in stark contrast to krypton, which may not be fractionated at all: atmospheric Kr is slightly heavier than solar Kr (at about 0.5% per amu), but it is the same as in carbonaceous chondrites [1]. Nonradiogenic xenon is also underabundant relative to krypton (the so-called "missing xenon" problem). Together these observations – the subject of Figure 1 – imply that xenon has been subject to fractionating escape and krypton not.

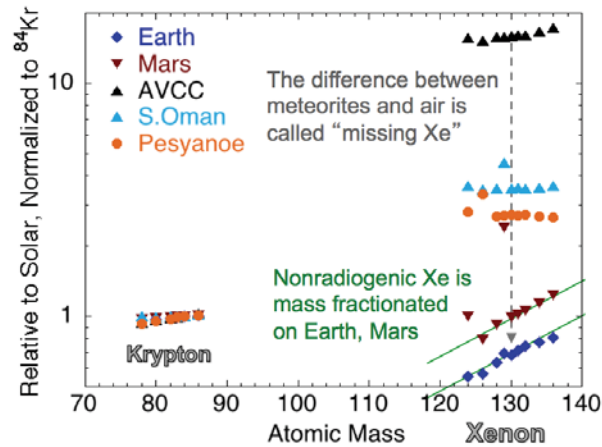


Figure 1. Xenon depletion and fractionation imply that Xe has escaped from Earth and Mars. Here isotopic abundances are normalized to ⁸⁴Kr. Pesyanoe and S. Oman are enstatite chondrites; AVCC denotes average carbonaceous chondrites [2]. Mars is from SNCs, solar from gases implanted by the solar wind.

Xenon alone among the noble gases can escape from planetary atmospheres as an ion. This is possible in hydrodynamic hydrogen escape because the hydrogen is partly ionized by incident solar UV. Provided that the H⁺ ions can also escape, as will happen in the absence of a magnetic field or, if the planetary magnetic field is strong, along open field lines as a polar wind. The strong Coulomb interaction between the ions couples heavy ions to the outflowing H⁺ ions much more strongly than the billiard ball collisions that couple neutrals. This is the subject of Figure 2. Xenon is a good candidate for this kind of escape because it is likely to be ionized. Xenon (12.1 eV, $\lambda < 102$ nm) is more easily ionized than H (13.6 eV, $\lambda < 91$ nm). Thus Xe can be ionized by solar UV. By contrast Kr (14.0 eV) is more difficult to ionize than H, so that nearly all the photons that might ionize it are absorbed by hydrogen. Kr⁺ can also be rapidly lost by reaction with H₂: Kr⁺ + H₂ → HKr⁺ + H followed by dissociative recombination HKr⁺ + e⁻ → Kr + H. Xe⁺ does not react with H₂, and is therefore longer-lived. The chief loss of Xe⁺ is radiative recombination, Xe⁺ + e⁻ → Xe + hν, which is slow. Thus Xe can be ionized when Kr is not.

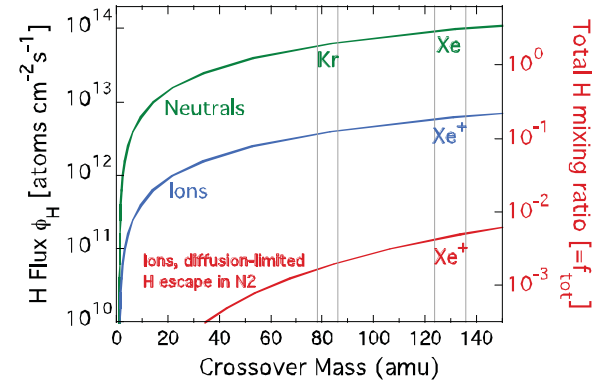


Figure 2. Hydrogen-flux thresholds for Kr, Xe, and Xe⁺ to escape in a partially ionized hydrogen-rich planetary wind. Two cases are shown, one (labeled "Ions" and "Neutrals") for Kr, Xe, and Xe⁺ escape from a predominantly H₂ atmosphere (appropriate to possible primary atmospheres), and the other for diffusion-limited escape of hydrogen through an N₂ atmosphere, as would be more appropriate for the Archean. For the latter the right-hand-axis indicates the corresponding hydrogen mixing ratio.

Conventional models posit that xenon escapes as a neutral [2,3]. This requires a very large hydrogen flux. In the energy limit, $\phi_H \approx 3 \times 10^{11} S_{EUV} \text{ cm}^{-2} \text{ s}^{-1}$, where S_{EUV} is the solar EUV radiation relative to today. Roughly, $S_{EUV} \propto t^{-1}$ in sunlike stars, so that $S_{EUV} > 300$, required for neutral Xe to escape, is likely restricted to times before 100 Myrs. Thus most discussions of fractionation by hydrodynamic escape focus on very young planets. By contrast escape of Xe^+ is possible with $S_{EUV} > 20$ in H_2 to as little as $S_{EUV} \approx 1$ in a diffusion-limited wind. But even in the latter case the atmosphere needs to be at least 0.5% H_2 or 0.25% CH_4 .

Escape may occur in the presence of a strong dipole magnetic field. If present, a strong magnetic field divides an escaping hydrogen exosphere into two regimes. From the poles Xe^+ ions could escape if dragged away by H^+ ions. Field lines rooted nearer the equator form complete loops that trap ions, creating what Mestel (1961) named the "dead zone." Neutral hydrogen can diffuse through the dead zone to escape, but Xe cannot.

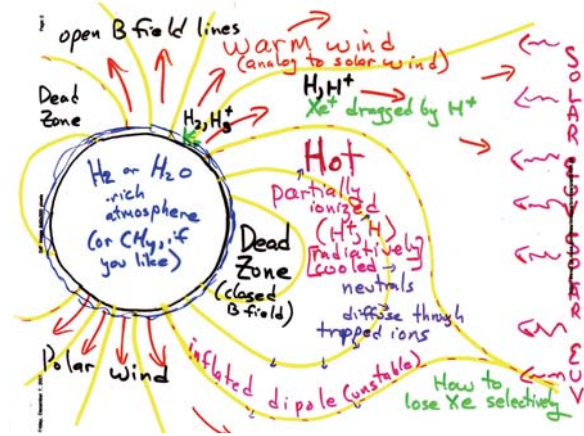


Figure 3. This cartoon from the archives illustrates the dipole magnetic field geometry and processes germane to Xe^+ escape from Earth. Field lines rooted near the poles allow an ionic planetary wind to flow into space.

Was fractionating xenon escape a sign of the times? In 1976 Srinivasan [4] found that the nonradiogenic xenon in a ~3.5 Ga Archean barite (BaSO_4) preserved an isotopic pattern about midway between the unfractionated solar or meteoritic pattern and what is present in the modern atmosphere. Pujol et al [5] replicated this result in a different barite from a drill core, and followed this up by measuring a distinctively light isotopic pattern in a fluid inclusion in a ~3 Ga quartz [6] (Figure 4). Pujol et al [6] propose that these

different xenons represent a true record of the changing composition of Earth's atmospheric xenon (Figure 5). If they are right, xenon was fractionated by a process that took place on Earth throughout the Archean. For Xe to escape in the Archean requires a considerable hydrogen escape rate. Ultimately the hydrogen comes from water, and is plausibly responsible for the oxygenation of the Earth.

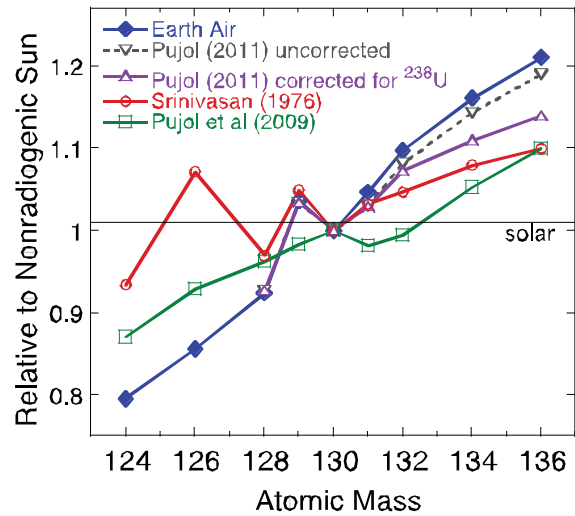


Figure 4. Xenon in 3.0-3.5 Ga Archean barites [4,5] and quartzes [6] is less fractionated than in modern air. If these are samples of ancient air, Xe escape from Earth is not a feature of Earth's earliest atmosphere but rather took place in the Archean.

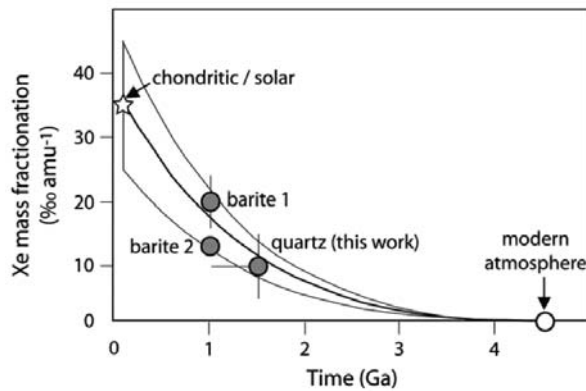


Figure 5. Screenshot of the tentative history of Xe fractionation *with respect to air* proposed by [6].

References: [1] Pepin R. O. (2006) EPSL 252, 1-14. [2] Pepin, R.O. (1991) Icarus 92, 2-79. [3] Sasaki S. and Nakazawa K. (1988) EPSL 89, 323-334. [4] Srinivasan B. (1976) EPSL 31, 129-141. [5] Pujol M. et al (2009) GCA 73, 6834-6846. [6] Pujol M. et al (2011) EPSL 308, 298-306.